INTERLABORATORY STUDY 88-2A

VALIDATION OF A METHOD FOR RESIN AND FATTY ACIDS

AMPOULES FOR SPIKING

REAGENT WATER AND

DIRECT METHYLATION

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Report Prepared by:
Laboratory Services Branch
Ontario Ministry of the Environment

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1 OVERVIEW OF THE INTERLABORATORY STUDIES TO ASSESS THE METHOD FOR RESIN AND FATTY ACIDS

In 1987, an Analytical Working Group (AWG) was formed to develop an improved analytical procedure for the analysis of Resin and Fatty Acids (MISA Group 26 and PP3). The AWG consisted of representatives from the Ontario Forest Industries Association (OFIA), Ontario Ministry of the Environment (MOE), and Environment Canada (EC), under the MISA program.

Initial work was done during 1987 to assess the stability of standards, the pH adjustments to be made prior to extraction, column conditions, and other instrumental conditions. The results have been reported elsewhere (3). In May 1988, the Method for Resin and Fatty Acids, Draft 3 (4) was ready to be validated by means of an interlaboratory collaborative study. A series of four separate studies were undertaken to assess the new method.

Interlaboratory Study 88-2A (This Report)

This was the first study initiated to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). Ampoules were distributed in June 1988. Four ampouled standards were provided to each participant, two to be spiked into reagent water and processed through the entire method, and two for direct methylation and injection into the analytical instrument.

The results indicated that the Draft Method produces similar results from all of the participants. Differences between laboratories may be attributed to differences in calibration of Dehydroabietic Acid. Some parameters are not recovered as well as others. This may be due to the difficulty of assuring the purity of the standards.

The results from Interlaboratory Study 88-2A demonstrated that the Draft Method works, as long as the calibration of Dehydroabietic Acid is carried out in a precise and accurate manner. The initial review of the raw data raised concern among the AWG regarding the use of two different solvents to prepare the standard solutions. A small follow-up study was required (see Interlaboratory Study 88-2B below), using fresh stock solutions, to assess whether some of the differences in performance were introduced by the different solvents used to prepared the standards.

Interlaboratory Study 88-2B

This was the second study to validate the performance of the Method for Resin and Fatty Acids, and was the follow-up to Interlaboratory Study 88-2A. Ampoules were distributed in August 1988. Four laboratories received two ampouled standards for direct methylation and instrumental injection. Each ampouled standard consisted of three parameters, one standard prepared in methanol and one standard prepared in methyl-t-butyl ether (MTBE). A third ampouled standard, consisting of the same three parameters dissolved in MTBE, but pre-methylated prior to sealing in the ampoules, was also provided to each laboratory. The third standard was to be used to verify that the four laboratories agreed in their calibration.

The results demonstrated that there was no significant difference between the mean of the results from standard prepared in methanol versus the mean of the results from the standard prepared in MTBE.

There was also no significant difference between the mean of the results from the standard prepared in MTBE that was not pre-methylated, versus the mean of the results from the standard prepared in MTBE that was pre-methylated.

Interlaboratory Study 88-3

This was the third interlaboratory study to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). A set of ten samples was distributed to the participants in November 1988. The sample sets consisted of a High Spike, Low Spike, and Blank of Reagent Water, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #1, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #2, and one unspiked Pulp and Paper Mill Effluent #3.

The results indicated that the laboratories were able to recover the spiked Resin and Fatty Acids from the reagent water samples. Results from the two different spiked pulp and paper mill effluents produced very variable results, with very few laboratories reporting results from the low spike effluent samples. Reasonable consistency of results between laboratories was achieved for the unspiked Pulp and Paper Mill Effluent #3.

The variability of the results suggested that there may have been problems recovering the spiked Resin and Fatty Acids from the effluent samples. It was decided to repeat this study in the spring of 1989. This study was reported as Interlaboratory Study 89-2 (see below).

Interlaboratory Study 89-2

This was the fourth (and final) interlaboratory study to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). A set of nine samples was distributed to the participants in March 1989. The sample sets consisted of a High Spike, Low Spike, and Blank in Reagent Water, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #1, a High Spike, Low Spike, and Blank of Pulp and Paper Mill Effluent #2.

The results indicated that the laboratories were able to recover the spiked Resin and Fatty Acids from the reagent water samples. Results from the two different spiked pulp and paper mill effluents produced very variable results, with very few laboratories reporting results from Pulp and Paper Mill Effluent #2. The same sources of pulp and paper mill effluent were used for both Interlaboratory Study 88-3 and this study (89-2). After reviewing the mill processes, it was noted that Pulp and Paper Mill Effluent #2 was a biologically treated effluent. The absence of recovery of the spiked Resin and Fatty Acids from this effluent in both studies, suggests that the effluent was still biologically active and degraded the spiking material.

Separate reports have been prepared for each study.

2 SUMMARY AND CONCLUSIONS

Interlaboratory Study 88-2A was designed to validate the performance of the Method for Resin and Fatty Acids, Draft 3 (4). It was initiated by the Quality Assurance Office, Laboratory Services Branch of the Ontario Ministry of the Environment, at the request of the Analytical Working Group (AWG) of the Pulp and Paper Sector under the MISA program.

Participants of Interlaboratory Study 88-2A were provided with a set of four ampouled standards, two to be spiked in reagent water and processed through the entire analytical method, and two for direct methylation and instrumental analysis. All materials were prepared by the staff of the Quality Assurance Office, Laboratory Services Branch. Nine laboratories initially agreed to participate in the study. Results were reported from seven participants.

This method is calibrated in terms of the response factor to Dehydroabietic Acid (DHA), due to the known instability and impurity of the other Resin and Fatty Acids. Initial review of the raw data suggested the presence of laboratory or analyte induced biases. To remove laboratory induced bias, the mean recovery for each parameter from each participant was normalized, relative to DHA, to compare the results between laboratories. The normalized results demonstrated consistent performance for Sandaracopimaric, Isopimaric, 9,10-Dichlorostearic, Chlorodehydroabietic, and Dichlorodehydroabietic Acids. Less consistent performance was noted for Oleic, Abietic, Neoabietic, Palustric, Levopimaric, and Linolenic Acids.

The results from this study demonstrate that the Draft Method performs consistently between laboratories for the analysis of Resin and Fatty Acids. Dehydroabietic Acid (DHA) is an acceptable reference material for calibration. The purity and accuracy of the DHA standard used by a laboratory is critical to producing good results with the Draft Method. Between laboratory variability is introduced by the differences in calibration of DHA, not the procedures of the Draft Method.

The greater variability of the results from the spiked reagent water samples may have been due to deterioration of the stock standard solution in Ampoules A and B (the solution had been prepared 6 months prior to the initiation of Interlaboratory Study 88-2A). A difference in the solvents (Ampoules A and B were prepared in methanol, Ampoules C and D were prepared in methyl-t-butyl ether) may have contributed to the difference in performance between the ampoules used for the spiked reagent water samples and the ampoules for direct methylation and instrumental analysis. A follow-up study was undertaken to determine if the different solvents affected the performance of the Draft Method, and was reported as Interlaboratory Study 88-2B. This follow-up study discounted the differences in performance due to the solvent.

3 INTRODUCTION

Interlaboratory Study 88-2A was designed to validate the analytical performance of the Method for Resin and Fatty Acids, Draft 3 (4) using ampouled standards. The participating laboratories were provided with two ampoules to methylate and inject directly into the analytical instrument, and two ampoules to spike into reagent water and process through the complete method.

Nine laboratories were invited to participate in this study: 3 government laboratories (provincial and federal), 2 industrial laboratories, and 4 commercial laboratories. The invited participants were required to agree to use the Draft Method for the analysis of the provided materials. Not all of the participants were able to report final results for all of the ampoules submitted (see Section 4.4). A list of participants is included in Appendix 2.

Details of ampoule preparation and distribution are given in Sections 4.1 and 4.2. Analytical methodology and data handling are presented in Sections 4.3. and 4.4. Final results are presented and discussed in Section 5.0. Each participant was assigned a unique identification code to maintain confidentiality.

4 PROCEDURE

4.1 Preparation of Ampoules

A 20 ±1 mg/L Resin and Fatty Acid (RFA) solution, consisting of the parameters listed in Table 1, was prepared in methanol. The RFA solution was subsequently chilled to -20 degrees Celcius prior to transferring to 5 mL amber ampoules. The solution was transferred via an automatic ampoule sealer and sealed with a flame. This solution was labelled RFA001.

The parameter list includes compounds that are not in MISA Test Groups 26 or PP3. These compounds were included in this study to evaluate the range of parameters that the method could be applied to. Pimaric Acid, which is in MISA Group 26, was not included in this ampoule, as the standard was temporarily unavailable from the supplier. A list of the parameters in MISA Test Groups 26 and PP3 is included in Appendix 2 for information purposes.

Ampoule RFA001 was used by representatives of the AWG for a standards stability study. The results were reported elsewhere (3). The results from this study indicated that the parameters were stable for at least a period of six months. Members of the AWG agreed that this ampoule was suitable to be used as the high standard to be spiked into reagent water and the appropriate number were labelled as Ampoule A for Round Robin 88-2A.

Based on the stability study mentioned above, it was accepted that the low standard to be used for spiking in reagent water could be prepared from Ampoule RFA001 for Interlaboratory Study 88-2A. A 2.0 ±0.1 mg/L solution was prepared from one RFA001 ampoule, in methanol.

Aliquots of the solution were manually transferred to amber ampoules using a 5 mL microlitre syringe and sealed using an automatic ampoule sealer. These ampoules were labelled as Ampoule B for Interlaboratory Study 88-2A.

TABLE 1 - Parameter List RFA001 and Ampoules A and B

Sandaracopimaric Acid
Isopimaric Acid
Palustric Acid
Levopimaric Acid
Dehydroabietic Acid
Abietic Acid
Neoabietic Acid
Chlorodehydroabietic Acid
Dichlorodehydroabietic Acid
Oleic Acid
Linolenic Acid
9,10-Dichlorostearic Acid

A more concentrated solution was required for the standards to be used for direct methylation and injection. A new 1000 µg/mL stock solution, using the same parameter list as in Table 1, was prepared using Methyl-t-butyl ether (MTBE) as the solvent. MTBE is the solvent used for the instrument calibration standards (4). As each compound was added to the volumetric flask, it was noted that each one dissolved almost immediately, except for Linolenic Acid. This compound was different from the others in that it was of a "gummy" consistency, rather than dry crystals. The flask was filled approximately three-quarters full with MTBE, a magnetic stirrer was added, the flask capped, and left to stir overnight to dissolve the compounds. The following day it was noted that a solid clump had formed of the undissolved Linolenic Acid. In an attempt to dissolve this compound, the solution was gently heated. After unsuccessfully attempting to dissolve the Linolenic Acid, it was decided to make a fresh solution and not include Linolenic Acid.

A fresh 1000 µg/mL solution was prepared in MTBE the following day. The solution was transferred manually to 5 mL amber ampoules, after cooling to -20 degrees Celcius, using a 5 mL microlitre syringe. An attempt was made to seal the ampoules using an automatic ampoule sealer. However the MTBE was more volatile than the methanol used for Ampoules A and B, and the vapor pressure from the ether caused the soft hot glass seal to pop. The solution was transferred from each ampoule back to the volumetric flask to be remixed, transferred again to new 5 mL amber ampoules, and manually sealed. Some solvent loss occurred during this procedure, so it was expected that the solution would be more concentrated. These ampoules were labelled Ampoule C for Interlaboratory Study 88-2A.

A low standard for direct methylation and injection was prepared from the 1000 µg/mL solution prior to its being sealed in the ampoules. A 25 µg/mL solution was prepared using MTBE as

the solvent. The solution was manually transferred into 5 mL amber vials using a 5 mL microlitre syringe. The ampoules were sealed manually and labelled as Ampoule D for Interlaboratory Study 88-2A. The parameter list for Ampoules C and D is given in Table 2.

RFA001 (Ampoule A) was originally prepared in November 1987 and considered acceptable by the members of the AWG for the interlaboratory study. Ampoule B was prepared in June 1988 from one of the RFA001 ampoules. Ampoules C and D were prepared in June 1988.

TABLE 2 - Parameter List
Ampoules C and D

Sandaracopimaric Acid
Isopimaric Acid
Palustric Acid
Levopimaric Acid
Dehydroabietic Acid
Abietic Acid
Neoabietic Acid
Chlorodehydroabietic Acid
Dichlorodehydroabietic Acid
Oleic Acid
9,10-Dichlorostearic Acid

4.2 Ampoule Distribution

The invited participants received a letter of notification in May, 1988. A copy is included in Appendix 2. All laboratories verified their participation by telephone. A list of invited participants is included in Appendix 2.

A set of four ampoules, one each of Ampoules A, B, C, and D, were packaged in a styrofoam shipping container and shipped via Purolator courier on June 7, 1988. The participants in Ontario, Quebec, and Nova Scotia all received their ampoule sets the following day. An error was made in the shipping bill for the package to be sent to British Columbia, so that the package was not received until one week later. To maintain the confidential identity of each participant, any time delay effects have not been discussed in Section 5.

Each package included a cover letter, an instruction sheet, and a report form. Copies are included in Appendix 2.

4.3 Analytical Methodology

All invited participants had agreed to use the Draft Method for Resin and Fatty Acids (4), a copy of which was provided to each participant with the letter of notification. All participants were asked to provide details of any problems they may have encountered with the method, and any subsequent modifications. Each participant was asked to analyze each ampoule in duplicate.

4.4 Data Handling

Results were submitted to the Quality Assurance Office of the Laboratory Services Branch, MOE in written form, using the provided forms. All data were then entered by laboratory code into an electronic spreadsheet. Blank spaces were left when a laboratory did not report results for a parameter that was present in the ampoules (i.e. the participant did not have the appropriate calibration standard). A value of "0" was used for the purpose of numerical evaluation for values reported as "Not Detected" by the laboratories.

One industrial laboratory was unable to perform the analyses due to staff shortages. One commercial laboratory was unable to complete the analyses due to an unexpected increase in workload. Final percent participation was 78%. However, the results from Laboratory 6002 were excluded from the statistical calculations as the laboratory used a different analytical technique from that specified in the Draft Method. Laboratory 6002 used GC/MS instead of GC/FID for the analysis of the extracts. Their results are included separately in Table 1 in Appendix 1, but are not part of the calculations.

Between-laboratory variability was determined by calculating the mean and standard deviation of the results reported. The minimum, maximum, and median values were also identified to give an indication of the range. Outliers were not removed from the data set when calculating between-laboratory variability. All results are presented in Appendix 1.

Results were converted to percent recovery based on the design value of the ampoules. These values are presented in Table 2 in Appendix 1.

To compare the performance of the different parameters from each participant, each result expressed as percent recovery was normalized, relative to that laboratory's results for Dehydroabietic Acid (DHA). DHA was used for these calculations as all the analytical results are calculated using the relative response factor of this parameter (4). These results are presented in Table 3 in Appendix 1.

Included in Appendix 1 are bar graphs of the recovery for each parameter from each participating laboratory (Figures 1-10). Each graph represents a different parameter, with each bar representing the results from a different participant. Outliers were not deleted from the data set when preparing the graphs. The mean value of the duplicates from each laboratory has been normalized relative to the laboratory's own result for DHA, the parameter used for calibration by each participant. Figure 11 in Appendix 1 is a bar graph of the percent recovery (relative to the design value) of DHA from all of the participants for each ampoule.

5 RESULTS AND DISCUSSION

The raw data in Table 1 (Appendix 1) was transformed into percent recovery data (Table 2, Appendix 1) using the design values for each parameter. This permitted a preliminary evaluation for the presence of unusual variability in the data for a given parameter, or for a given laboratory. The results suggested the presence of analyte or laboratory induced bias. Thus Abietic Acid was noticeably under-recovered by all of the participants, and Laboratory 6008 under-recovered more frequently than the other participants.

Bias that is consistent across several parameters suggests a laboratory related calibration or recovery problem. Bias consistent for a given parameter across several laboratories suggests a problem with the theory of a constant response relative to DHA, or an error in the ampoule design value. In order to remove the effect of differences in laboratory calibration, all parameter recoveries were normalized against the individual laboratory's recovery for DHA. If the normalized interlaboratory recovery for a parameter was more consistent, then:

a) the method is reliable and precise, and

b) the observed variable recovery across parameters may reflect the anticipated problems of obtaining pure, stable standards for Resin and Fatty Acids.

Figures 1 - 10 display the normalized percent recovery results. The findings are summarized in Table 3.

The data summarized in Table 3 accentuates the generally good performance of the Draft Method between laboratories, if DHA is taken as the reference point. The raw data (Tables 1 and 2, Appendix 1) suggested a possible difference between Ampoules A and B (High and Low Spikes, Reagent Water) versus Ampoules C and D (High and Low Standards, Direct Methylation). This was initially ascribed to either ampoule age, or solvent used, or both. The variable recovery was also initially attributed to a possible error in the preparation of the solutions or the unavailability of pure, stable materials for preparing the standards.

TABLE 3 - Assessment of Normalized Recovery (Relative to DHA)

Parameter	Ranking	Comments
Linolenic	Variable	Recovery 50-90%, Ampoules A and B only
Oleic	Extremely variable	Recovery 50-200% Ampoules A and B Recovery 30-50% Ampoules C and D
Sandaracopimaric	Very consistent	Recovery 70% Laboratory 6009 low for Ampoules C and D
Isopimaric	Consistent	Recovery 80-100% Laboratories 6001 and 6008 high for all four ampoules Laboratory 6009 low for Ampoules C and D
Palustric/Levopimaric	Variable	Recovery 30-80% Laboratories 6001 and 6008 high for all four ampoules Laboratory 6009 low for Ampoules C and D
Abietic	Consistent	Recovery 20-30% for Ampoules A and B Recovery 40-60% for Ampoules C and D Laboratory 6009 low for Ampoules C and D
Neoabietic	Variable	Recovery 40-90% Laboratory 6009 very low for Ampoules C and D
9,10-Dichlorostearic	Consistent	Recovery 40-50% Laboratory 6009 low for Ampoules C and D
Chlorodehydroabietic	Consistent	Recovery 50% Laboratories 6004 and 6008 high for all four ampoules Laboratory 6009 low for Ampoules B, C, and D
Dichlorodehydroabietic	Consistent	Recovery 60-80% Laboratory 6009 low for Ampoules B, C, and D

The consistency of the normalized recovery for Sandaracopimaric, Isopimaric, 9,10-Dichlorostearic, Chlorodehydroabietic, and Dichlorodehydroabietic Acids, for all four ampoules, suggests that these materials and the Draft Method performed well. There is no dependence of solvent or laboratory. There may be a method related recovery problem for some the parameters, or a problem with the purity of the standards used.

Oleic and Abietic Acids showed a dependence on solvent, but in opposite directions. They are the most unstable parameters, with a low level of purity of the crystals.

Neoabietic, Palustric and Levopimaric, and Linolenic Acids were highly variable. Palustric and Levopimaric Acids co-elute, and all participants reported a combined result. The variability for these two parameters may be due to the partial separation on the gas chromatographic column observed by some participants, while others may have observed no separation. The variable behavior

of Neoabietic and Linolenic Acids may be due to a particular standard instability, or to a method deficiency which decreases the reliability of this data. The variability for all four parameters is independent of the solvent used.

If Ampoules A and B (older stock) had degraded, the normalized percent recovery data suggests that DHA and most of the other parameters degraded in a highly consistent pattern. This occurrence is less likely than the difficulties associated with ensuring the purity of the materials used to prepare the standards.

The results from this study demonstrate that the Draft Method performs consistently between laboratories for the analysis of Resin and Fatty Acids. Dehydroabietic Acid (DHA) is an acceptable reference material for calibration. The purity and accuracy of the DHA standard used by a laboratory is critical to producing good results with the Draft Method. Between laboratory variability is introduced by the differences in calibration of DHA, not the procedures of the Draft Method.

The preliminary review of the data set (Table 1, Appendix 1) had raised concerns by the AWG regarding the use of the different solvents to prepare the standards. A follow-up study was requested to assess the effect of the different solvents (methanol and MTBE) used to prepare the standard solutions. This study was conducted in August 1988 and reported as Interlaboratory Study 88-2B.

6 REFERENCES

1. Ontario Regulation 695/88 as amended to Ontario Regulation 533/89 under the Environmental Protection Act; Effluent Monitoring - General.

2. The Development Document for the Draft Effluent Monitoring Regulation for the Pulp and Paper Sector, March 1989; ISBN 0-7729-4764-3.

3. Minutes from the OFIA/MOE/EC Analytical Working Group, 1987 and 1988, inclusive. (Copies of all minutes were reported to the Joint Technical Committee for the Pulp and Paper Sector.)

4. Method for Resin and Fatty Acids; OFIA/MOE/EC Analytical Working Group; Draft, May 5, 1988.

7 APPENDIX 1 - FULL DATA SET

Table 1	Results for Round Robin 88-2A
Table 2	Results for Round Robin 88-2A, Expressed as Percent Recovery of the Design Value
Table 3	Mean Recovery Results Normalized to Dehydroabietic Acid, as Reported by Each Participant
Figure 1	Linolenic Acid Normalized to DHA
Figure 2	Oleic Acid Normalized to DHA
Figure 3	Sandaracopimaric Acid Normalized to DHA
Figure 4	Isopimaric Acid Normalized to DHA
Figure 5	Palustric & Levopimaric Acids Normalized to DHA
Figure 6	Abietic Acid Normalized to DHA
Figure 7	Neoabietic Acid Normalized to DHA
Figure 8	9,10-Dichlorostearic Acid Normalized to DHA
Figure 9	Chlorodehydroabietic Acid Normalized to DHA
Figure 10	Dichlorodehydroabietic Acid Normalized to DHA
Figure 11	Dichlorodehydroabietic Acid (Percent Recovery of Design Value

TABLE 1 - ROUND ROBIN 88-2A: RESULTS FROM RESIN AND FATTY ACID AMPOULES
RESULTS EXPRESSED AS ug/mL

DISTRIBUTED: JUNE 7, 1988 AMPOULE PARAMETER		DESIGN (ug/mL)	LABORATORY NUMBER 6001 #1	6001 #2	6004 #1	6005 #1	6005 #2	6007 #1	6007 #2	6008 #1	6008 #2	6009 #1	6009 #2	RANGE MEAN	MIN	MAX	MEDIAN	STD DEV	6002 #1	6002 #2
C	LINOLENIC	-	-	-	-	-	-	-	-	143	164	-	-						-	-
C	OLEIC	1004			597	305	292	284	287	421	401	590	590	418.6	284	597	401	139.3	850	860
C	SANDARACOPIMARIC	1007	1058	1036	855	972	924	876	894	751	743	900	900	900.8	743	1058	900	99.3	1020	1030
C	ISOPIMARIC	1004	1406	1386	1135	1320	1210	1196	1218	1160	1140	1160	1180	1228.3	1135	1406	1196	97.2	1200	1190
C	PALUSTRIC/LEVOPIMARIC	2009	2042	2002	1236	1936	1844	1566	1576	1400	1410	930	910	1532.0	910	2042	1566	401.7	630	650
C	DEHYDROABIETIC	1004	1270	1264	1255	1176	1136	1208	1224	1060	1070	1660	1680	1273.0	1060	1680	1224	209.1	1420	1430
C	ABIETIC	1006	686	680	531	654	636	630	640	585	603	450	440	594.1	440	686	630	85.6	2810	2890
C	NEOABIETIC	1004	1028	1018	714	1030	1000	880	896	735	745	260	240	776.9	240	1030	880	286.7	860	940
C	CHLORODEHYDROABIETIC	1005	616	628	1041	594	622	608	622	1230	1270	540	560	757.4	540	1270	622	278.4	1630	1640
C	9,10-DICHLOROSTEARIC	1008	630	640	709	596	604	612	612			530	520	605.9	520	709	612	56.7	520	530
C	DICHLORODEHYDROABIETIC	1003	804	812	944	854	856	902	900	872	905	680	660	835.4	660	944	856	91.5	1430	1450
C	PIMARIC	-	15.6	15.6																
C	*o-METHYLPODOCARPIC(%REC)		103.1%	59.9%	99.2%	106.0%	105.0%	88.0%	90.0%	87.0%	94.6%	97.0%	97.0%						105.3%	103.5%
D	LINOLENIC	-	-	-	-	-	-	-	-	25.2	21.2	-	-						-	-
D	OLEIC	251			142	102	122	135.8	130.8	108	101	140	140	124.6	101	142	130.8	16.9	140	150
D	SANDARACOPIMARIC	252	284	278	204	220	214	224	222	192	182	220	220	223.6	182	284	220	31.4	190	160
D	ISOPIMARIC	251	380	370	258	330	310	292	290	296	267	290	265	304.4	258	380	292	40.6	210	260
D	PALUSTRIC/LEVOPIMARIC	502	552	534	232	442	428	360	356	310	281	150	145	344.5	145	552	356	138.3	110	140
D	DEHYDROABIETIC	251	348	328	331	272	266	308	314	275	260	440	370	319.3	260	440	314	53.7	340	350
D	ABIETIC	252	187.6	179.4	111	150	146	152	148.6	130	123	100	105	139.3	100	187.6	146	28.7	590	740
D	NEOABIETIC	251	278	268	122	234	226	196.8	192.4	103	82.9	40	40	162.1	40	278	192.4	87.9	120	83
D	CHLORODEHYDROABIETIC	251	171	166.4	246	138	136	146.2	157.2	302	287	130	135	183.2	130	302	157.2	63.8	330	370
D	9,10-DICHLOROSTEARIC	252	173.6	165	195	134	138	146	145			130	130	150.7	130	195	145	22.5	76	80
D	DICHLORODEHYDROABIETIC	251	224	210	222	204	206	218	222	220	220	160	155	205.5	155	224	218	24.7	300	340
D	*o-METHYLPODOCARPIC(%REC)		110.4%	105.1%	100.2%	97.0%	97.0%	90.0%	90.0%	88.2%	95.0%	96.0%	93.0%						113.6%	111.4%

AMPOULE C: HIGH STANDARD FOR DIRECT METHYLATION AND INJECTION
AMPOULE D: LOW STANDARD FOR DIRECT METHYLATION AND INJECTION

NOTE: FOR EACH PARTICIPANT, #1 = REPLICATE 1, #2 = REPLICATE 2
* o-METHYLPODOCARPIC IS SURROGATE STANDARD

RESULTS FROM LAB 6001 ARE NOT INCLUDED
IN THE SUMMARY STATISTICS
AS THEY USED A DIFFERENT DETECTOR FROM THAT
SPECIFIED IN THE DRAFT METHOD.

TABLE 1 - INTERLABORATORY STUDY 88-2A: RESULTS FROM RESIN AND FATTY ACID AMPOULES
RESULTS EXPRESSED AS ug/L

DISTRIBUTED: JUNE 7, 1988		DESIGN	LABORATORY NUMBER 6001		6004	6005		6007		6008		6009		RANGE					6002	
AMPOULE	PARAMETER	(ug/L)	#1	#2	#1	#1	#2	#1	#2	#1	#2	#1	#2	MEAN	MIN	MAX	MEDIAN	STD DEV	#1	#2
A	LINOLENIC	408	434			329	333	325	325	217	194	375	375	323.0	194	434	329	75.6	320	290
A	OLEIC	420	484		876	422	431	344	276	196	161	465	480	413.5	161	876	426.5	200.3	1560	1330
A	SANDARACOPIMARIC	432	411		418	374	388	342	342	273	240	385	385	355.8	240	418	379.5	58.3	830	830
A	ISOPIMARIC	416	534		514	497	521	454	451	382	344	485	495	467.7	344	534	480	61.8	1270	1170
A	PALUSTRIC/LEVOPIMARIC	824	762		592	671	676	528	531	292	285	580	610	552.7	285	762	586	156.1	650	660
A	DEHYDROABIETIC	428	487		588	463	471	478	491	392	341	495	495	470.1	341	588	482.5	65.6	1470	1340
A	ABIETIC	406	137		144	128	129	120	122	93.9	82.3	125	130	121.1	82.3	144	126.5	18.9	2020	1970
A	NEOABIETIC	410	382		344	352	344	280	284	161	156	285	305	289.3	156	382	295	76.8	700	750
A	CHLORODEHYDROABIETIC	412	240		476	239	249	224	214	365	393	225	225	285.8	214	476	239.5	91.9	1680	1550
A	9,10-DICHLOROSTEARIC	404	242		348	235	224	207	155			220	220	231.4	155	348	222	54.1	580	490
A	DICHLORODEHYDROABIETIC	406	310		420	332	319	324	253	284	244	265	270	302.1	244	420	297	51.8	1970	1370
A	Ko-METHYLPODOCARPIC(%REC)		102.9%		104.6%	95.0%	96.0%	87.0%	89.0%	90.0%	77.8%	91.0%	95.0%						84.8%	89.5%
B	LINOLENIC	40.8				21	16	34.2	34.3	17.4	19.5	35	35	26.6	16	35	27.6	8.8	20	28
B	OLEIC	42			84.6	40	41	44.6	53.1	23.5	26.8	115	145	63.7	23.5	145	44.6	42.1	160	160
B	SANDARACOPIMARIC	43.2	38.4	38.1	41.6	36	36	34.1	34	28.7	26.3	40	40	35.7	26.3	41.6	36	4.8	690	710
B	ISOPIMARIC	41.6	52.4	50.8	49.6	53	57	43.8	44.1	45.1	39.5	50	50	48.7	39.5	57	50	5.0	79	75
B	PALUSTRIC/LEVOPIMARIC	82.4	70	67.5	47.4	56	57	42.7	41	27	27.5	50	50	48.7	27	70	50	14.0	37	30
B	DEHYDROABIETIC	42.8	46.8	46.7	62.6	48	47	54.8	53.6	45.7	39.9	55	55	50.5	39.9	62.6	48	6.3	140	150
B	ABIETIC	40.6	13.4	14.4	18.6	11	11	10.5	11.8	8.87	8.14	10	10	11.6	8.14	18.6	11	2.9	160	170
B	NEOABIETIC	41	35.6	32.7	22	28	29	21.5	27	12.2	10.9	25	25	24.4	10.9	35.6	25	7.6	47	32
B	CHLORODEHYDROABIETIC	41.2	24.6	19.2	45.8	20	20	21.9	21.3	164	91.8	10	10	40.8	10	164	21.3	46.9	130	140
B	9,10-DICHLOROSTEARIC	40.4	23.7	24.5	31	20	19	23	23			20	20	22.9	19	33	23	4.3	33	33
B	DICHLORODEHYDROABIETIC	40.6	31.3	28.6	42	30	28	28.2	30.8	35.4	27.4	10	10	27.4	10	42	28.6	9.6	110	120
B	Ko-METHYLPODOCARPIC(%REC)		99.9%	93.5%	94.4%	95.0%	97.0%	85.0%	87.0%	88.2%	77.9%	97.0%	100.0%						92.5%	83.7%

AMPOULE A: HIGH SPIKE IN REAGENT WATER
AMPOULE B: LOW SPIKE IN REAGENT WATER

NOTE: FOR EACH PARTICIPANT, #1 = REPLICATE 1, #2 = REPLICATE 2
* o-METHYLPODOCARPIC IS SURROGATE STANDARD

RESULTS FROM LAB 6002 ARE NOT INCLUDED
IN THE SUMMARY STATISTICS
IF THEY USED A DIFFERENT DETECTOR FROM THAT

TABLE 2 - INTERLABORATORY STUDY 88-2A: RESULTS FROM RESIN AND FATTY ACID AMPOULES
RESULTS EXPRESSED AS PERCENT RECOVERY OF DESIGN VALUE

DISTRIBUTED: JUNE 7, 1988		DESIGN	LAB NUMBER 6001		6004	6005		6007		6008		6009		MEAN	RANGE		MEDIAN
AMPOULE	PARAMETER	(ug/L)	#1	#2	#1	#1	#2	#1	#2	#1	#2	#1	#2		MIN	MAX	
A	LINOLENIC	408	106%			81%	82%	80%	80%	53%	48%	92%	92%	79%	48%	106%	81%
A	OLEIC	420	115%		209%	100%	103%	82%	66%	47%	38%	111%	114%	98%	38%	209%	102%
A	SANDARACOPIMARIC	432	95%		97%	87%	90%	79%	79%	63%	56%	89%	89%	82%	56%	97%	88%
A	ISOPIMARIC	416	128%		124%	119%	125%	109%	108%	92%	83%	117%	119%	112%	83%	128%	118%
A	PALUSTRIC/LEVOPIMARIC	824	92%		72%	81%	82%	64%	64%	35%	35%	70%	74%	67%	35%	92%	71%
A	DEHYDROABIETIC	428	114%		137%	108%	110%	112%	115%	92%	80%	116%	116%	110%	80%	137%	113%
A	ABIETIC	406	34%		35%	32%	32%	30%	30%	23%	20%	31%	32%	30%	20%	35%	32%
A	NEOABIETIC	410	93%		84%	86%	84%	68%	69%	39%	38%	70%	74%	71%	38%	93%	72%
A	CHLORODEHYDROABIETIC	412	58%		116%	58%	60%	54%	52%	89%	95%	55%	55%	69%	52%	116%	58%
A	9,10-DICHLOROSTEARIC	404	60%		86%	58%	55%	51%	38%			54%	54%	57%	38%	86%	55%
A	DICHLORODEHYDROABIETIC	406	76%		103%	82%	79%	80%	62%	70%	60%	65%	67%	74%	60%	103%	73%
B	LINOLENIC	40.8				51%	39%	84%	84%	43%	48%	86%	86%	65%	39%	86%	68%
B	OLEIC	42			201%	95%	98%	106%	126%	56%	64%	274%	345%	152%	56%	345%	106%
B	SANDARACOPIMARIC	43.2	89%	88%	96%	83%	83%	79%	79%	66%	61%	93%	93%	83%	61%	96%	83%
B	ISOPIMARIC	41.6	126%	122%	119%	127%	137%	105%	106%	108%	95%	120%	120%	117%	95%	137%	120%
B	PALUSTRIC/LEVOPIMARIC	82.4	85%	82%	58%	68%	69%	52%	50%	33%	33%	61%	61%	59%	33%	85%	61%
B	DEHYDROABIETIC	42.8	109%	109%	146%	112%	110%	128%	125%	107%	93%	129%	129%	118%	93%	146%	112%
B	ABIETIC	40.6	33%	35%	46%	27%	27%	26%	29%	22%	20%	25%	25%	29%	20%	46%	27%
B	NEOABIETIC	41	87%	80%	54%	68%	71%	52%	66%	30%	27%	61%	61%	60%	27%	87%	61%
B	CHLORODEHYDROABIETIC	41.2	60%	47%	111%	49%	49%	53%	52%	398%	223%	24%	24%	99%	24%	398%	52%
B	9,10-DICHLOROSTEARIC	40.4	59%	61%	82%	50%	47%	57%	57%			50%	50%	57%	47%	82%	57%
B	DICHLORODEHYDROABIETIC	40.6	77%	70%	103%	74%	69%	69%	76%	87%	67%	25%	25%	68%	25%	103%	70%

AMPOULE A: HIGH SPIKE IN REAGENT WATER
AMPOULE B: LOW SPIKE IN REAGENT WATER

NOTE: #1 - REPLICATE 1; #2 - REPLICATE 2

TABLE 2 - INTERLABORATORY STUDY 88-2A: RESULTS FROM RESIN AND FATTY ACID AMPOULES
RESULTS EXPRESSED AS PERCENT RECOVERY OF DESIGN VALUE

DISTRIBUTED: JUNE 7, 1988		DESIGN	LAB NUMBER 6001		6004	6005		6007		6008		6009		MEAN	RANGE		MEDIAN
AMPOULE	PARAMETER	(ug/mL)	#1	#2	#1	#1	#2	#1	#2	#1	#2	#1	#2		MIN	MAX	
C	OLEIC	1004			59%	30%	29%	28%	29%	42%	40%	59%	59%	42%	28%	59%	40%
C	SANDARACOPIMARIC	1007	105%	103%	85%	97%	92%	87%	89%	75%	74%	89%	89%	89%	74%	105%	89%
C	ISOPIMARIC	1004	140%	138%	113%	131%	121%	119%	121%	116%	114%	116%	118%	122%	113%	140%	119%
C	PALUSTRIC/LEVOPIMARIC	2009	102%	100%	62%	96%	92%	78%	78%	70%	70%	46%	45%	76%	45%	102%	78%
C	DEHYDROABIETIC	1004	126%	126%	125%	117%	113%	120%	122%	106%	107%	165%	167%	127%	106%	167%	122%
C	ABIETIC	1006	68%	68%	53%	65%	63%	63%	64%	58%	60%	45%	44%	59%	44%	68%	63%
C	NEOABIETIC	1004	102%	101%	71%	103%	100%	88%	89%	73%	74%	26%	24%	77%	24%	103%	88%
C	CHLORODEHYDROABIETIC	1005	61%	62%	104%	59%	62%	60%	62%	122%	126%	54%	56%	75%	54%	126%	62%
C	9,10-DICHLOROSTEARIC	1008	63%	63%	70%	59%	60%	61%	61%			53%	52%	60%	52%	70%	61%
C	DICHLORODEHYDROABIETIC	1003	80%	81%	94%	85%	85%	90%	90%	87%	90%	68%	66%	83%	66%	94%	85%
D	OLEIC	251			57%	41%	49%	54%	52%	43%	40%	56%	56%	50%	40%	57%	52%
D	SANDARACOPIMARIC	252	113%	110%	81%	87%	85%	89%	88%	76%	72%	87%	87%	89%	72%	113%	87%
D	ISOPIMARIC	251	151%	147%	103%	131%	124%	116%	116%	118%	106%	116%	106%	121%	103%	151%	116%
D	PALUSTRIC/LEVOPIMARIC	502	110%	106%	46%	88%	85%	72%	71%	62%	56%	30%	29%	69%	29%	110%	71%
D	DEHYDROABIETIC	251	139%	131%	132%	108%	106%	123%	125%	110%	104%	175%	147%	127%	104%	175%	125%
D	ABIETIC	252	75%	71%	44%	60%	58%	60%	59%	52%	49%	40%	42%	55%	40%	75%	58%
D	NEOABIETIC	251	111%	107%	49%	93%	90%	78%	77%	41%	33%	16%	16%	65%	16%	111%	77%
D	CHLORODEHYDROABIETIC	251	68%	66%	98%	55%	54%	58%	63%	120%	114%	52%	54%	73%	52%	120%	63%
D	9,10-DICHLOROSTEARIC	252	69%	65%	77%	53%	55%	58%	58%			52%	52%	60%	52%	77%	58%
D	DICHLORODEHYDROABIETIC	251	89%	84%	89%	81%	82%	87%	89%	80%	80%	64%	62%	82%	62%	89%	87%

AMPOULE C: HIGH STANDARD FOR DIRECT METHYLATION AND INJECTION
AMPOULE D: LOW STANDARD FOR DIRECT METHYLATION AND INJECTION

NOTE: #1 - REPLICATE 1; #2 - REPLICATE 2

TABLE 3 - RESULTS FROM INTERLABORATORY STUDY 88-2A
VALUES NORMALIZED TO DEHYDROABIETIC ACID
AS REPORTED BY EACH PARTICIPANT

AMPOULE	PARAMETER	DESIGN	LABORATORY NUMBER 6001	6004	6005	6007	6008	6009
A	9,10-DICHLOROSTEARIC	404	53%	63%	52%	40%		47%
B	9,10-DICHLOROSTEARIC	40.4	55%	56%	43%	45%		39%
C	9,10-DICHLOROSTEARIC	1008	50%	56%	52%	50%		31%
D	9,10-DICHLOROSTEARIC	252	50%	59%	50%	47%		32%
A	PALUSTRIC/LEVOPIMARIC	824	81%	52%	75%	57%	41%	62%
B	PALUSTRIC/LEVOPIMARIC	82.4	76%	39%	62%	40%	33%	47%
C	PALUSTRIC/LEVOPIMARIC	2009	80%	49%	82%	65%	66%	28%
D	PALUSTRIC/LEVOPIMARIC	502	80%	35%	81%	58%	55%	18%
A	CHLORODEHYDROABIETIC	412	51%	84%	54%	47%	107%	47%
B	CHLORODEHYDROABIETIC	41.2	49%	76%	44%	41%	310%	19%
C	CHLORODEHYDROABIETIC	1005	49%	83%	53%	51%	117%	33%
D	CHLORODEHYDROABIETIC	251	50%	74%	51%	49%	110%	33%
A	DEHYDROABIETIC	428	100%	100%	100%	100%	100%	100%
B	DEHYDROABIETIC	42.8	100%	100%	100%	100%	100%	100%
C	DEHYDROABIETIC	1004	100%	100%	100%	100%	100%	100%
D	DEHYDROABIETIC	251	100%	100%	100%	100%	100%	100%
A	DICHLORODEHYDROABIETIC	406	67%	75%	73%	63%	76%	57%
B	DICHLORODEHYDROABIETIC	40.6	68%	71%	64%	57%	77%	19%
C	DICHLORODEHYDROABIETIC	1003	64%	75%	74%	74%	84%	40%
D	DICHLORODEHYDROABIETIC	251	64%	67%	76%	71%	82%	39%

AMPOULE	PARAMETER	DESIGN	LABORATORY NUMBER 6001	6004	6005	6007	6008	6009
A	ISOPIMARIC	416	113%	90%	112%	96%	102%	102%
B	ISOPIMARIC	41.6	114%	82%	119%	83%	102%	94%
C	ISOPIMARIC	1004	110%	90%	109%	99%	108%	70%
D	ISOPIMARIC	251	111%	78%	119%	94%	105%	69%
A	LINOLENIC	408	93%	0%	74%	70%	59%	79%
B	LINOLENIC	40.8	0%	0%	41%	66%	45%	67%
A	NEOABIETIC	410	82%	61%	78%	61%	45%	62%
B	NEOABIETIC	41	76%	37%	63%	47%	28%	47%
C	NEOABIETIC	1004	81%	57%	88%	73%	69%	15%
D	NEOABIETIC	251	81%	37%	86%	63%	35%	10%
A	OLEIC	420	101%	152%	93%	65%	50%	97%
B	OLEIC	42	0%	138%	87%	92%	60%	241%
C	OLEIC	1004	0%	48%	26%	23%	39%	35%
D	OLEIC	251	0%	43%	42%	43%	39%	35%
A	ABIETIC	406	30%	26%	29%	26%	25%	27%
B	ABIETIC	40.6	31%	31%	24%	22%	21%	19%
C	ABIETIC	1006	54%	42%	56%	52%	56%	27%
D	ABIETIC	252	54%	33%	55%	48%	47%	25%
A	SANDARACOPIMARIC	432	84%	70%	81%	70%	69%	77%
B	SANDARACOPIMARIC	43.2	81%	66%	75%	62%	64%	72%
C	SANDARACOPIMARIC	1007	82%	60%	82%	73%	70%	54%
D	SANDARACOPIMARIC	252	83%	61%	80%	71%	70%	54%

NOTE: FOR AMPOULES A AND B: DESIGN VALUE IN ug/L
FOR AMPOULES C AND D: DESIGN VALUE IN ug/mL

FIGURE 1: INTERLABORATORY STUDY 88–2A

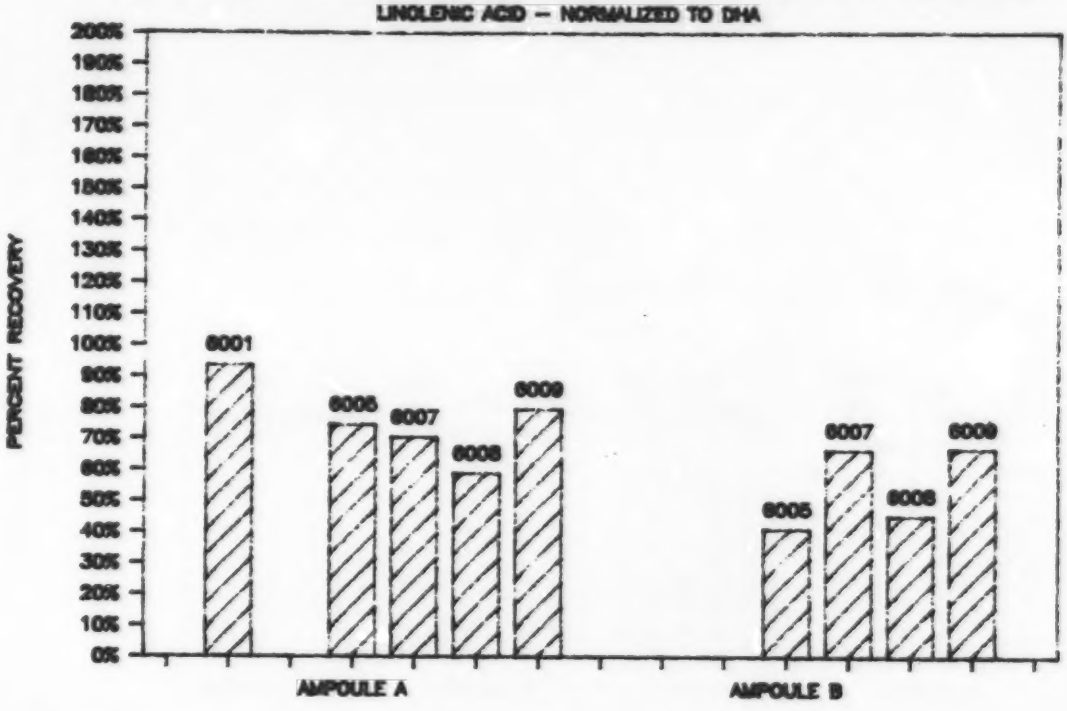


FIGURE 2: INTERLABORATORY STUDY 88–2A

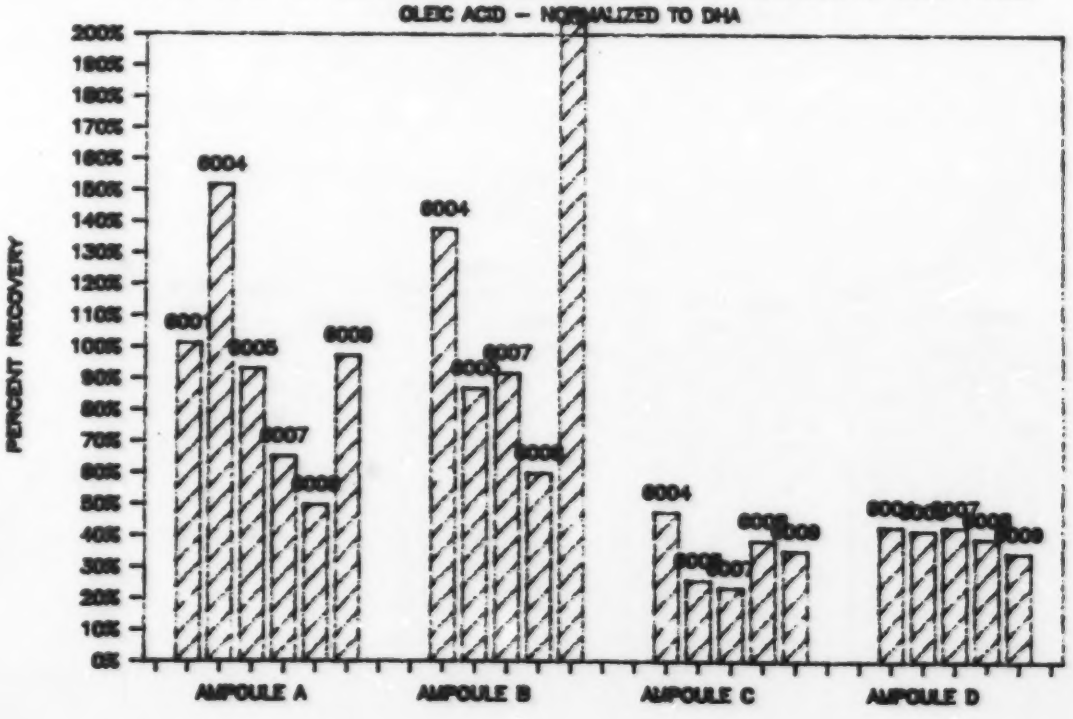


FIGURE 3: INTERLABORATORY STUDY 88–2A

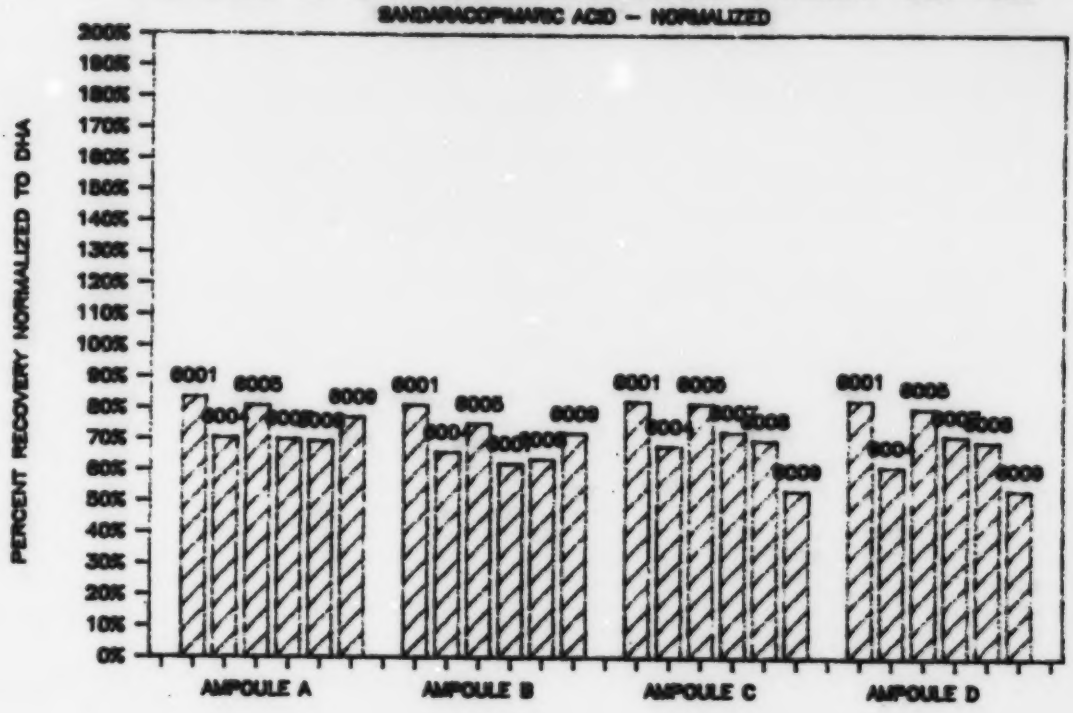


FIGURE 4: INTERLABORATORY STUDY 88–2A

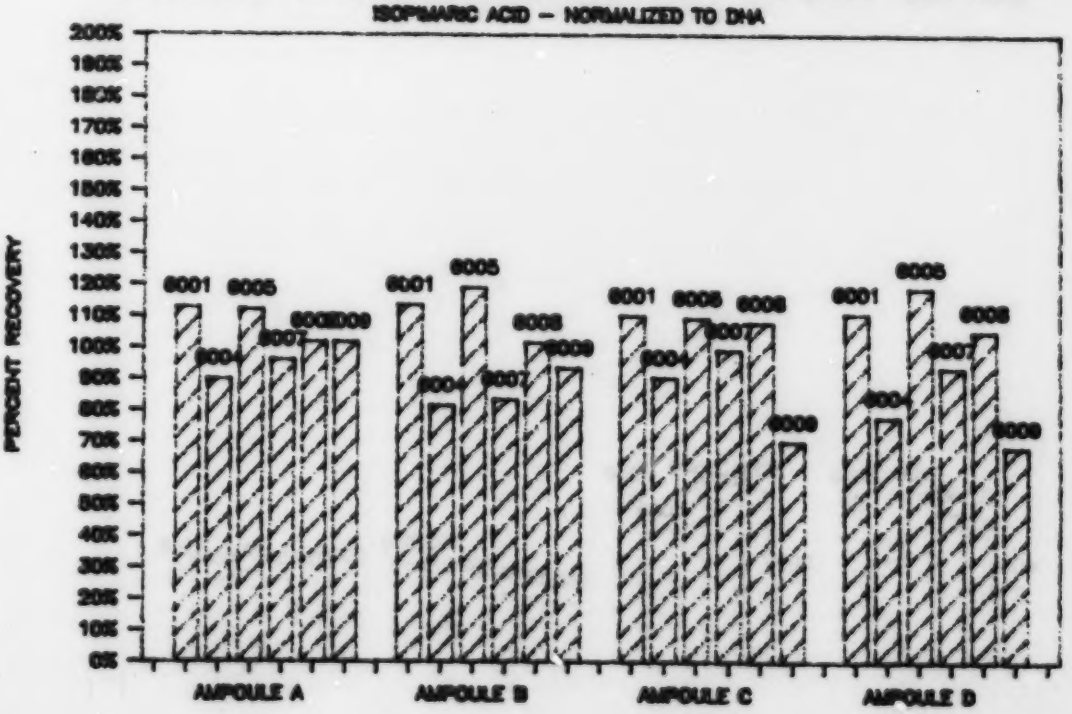


FIGURE 5: INTERLABORATORY STUDY 88–2A

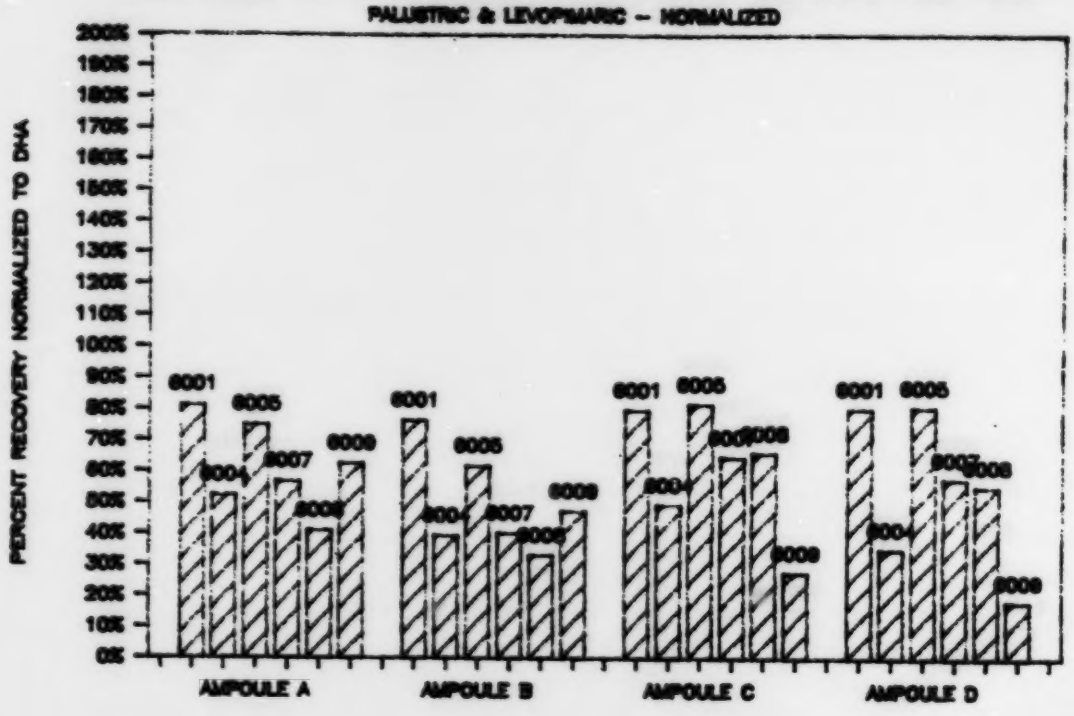


FIGURE 6: INTERLABORATORY STUDY 88–2A

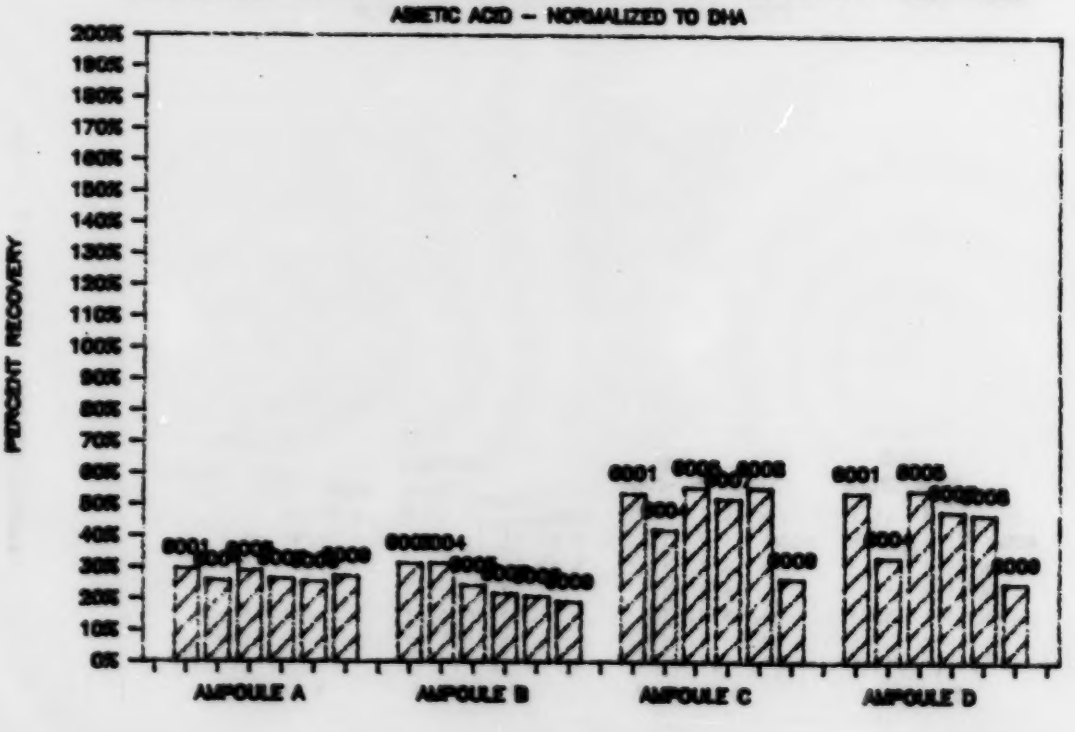


FIGURE 7: INTERLABORATORY STUDY 88-2A

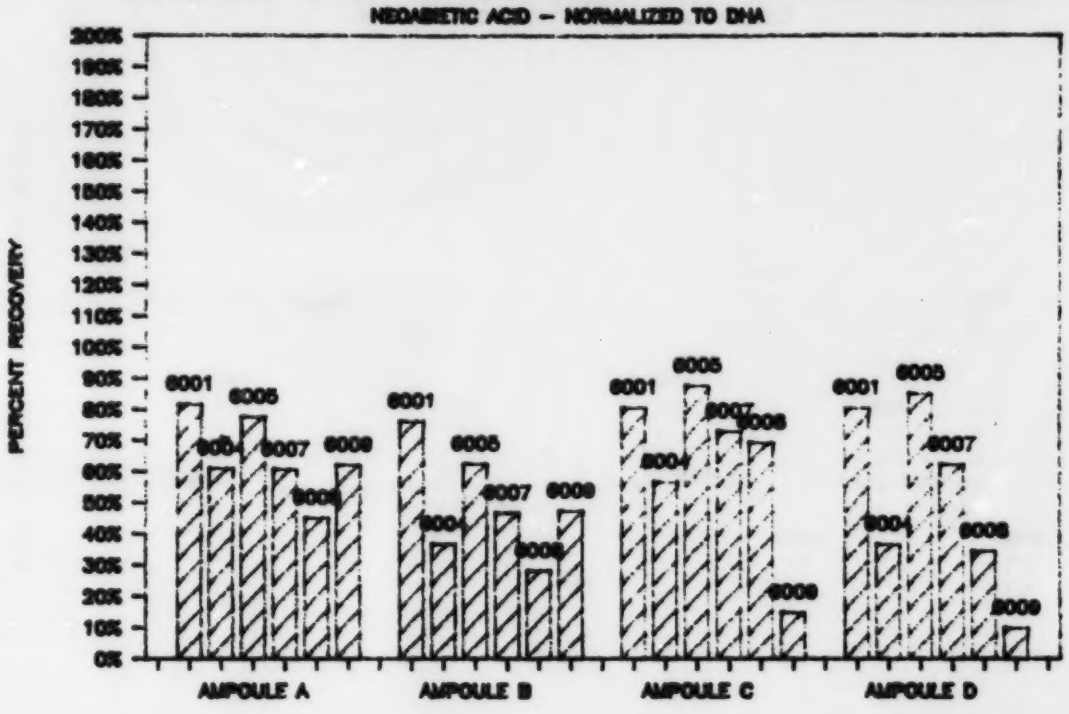


FIGURE 8: INTERLABORATORY STUDY 88-2A

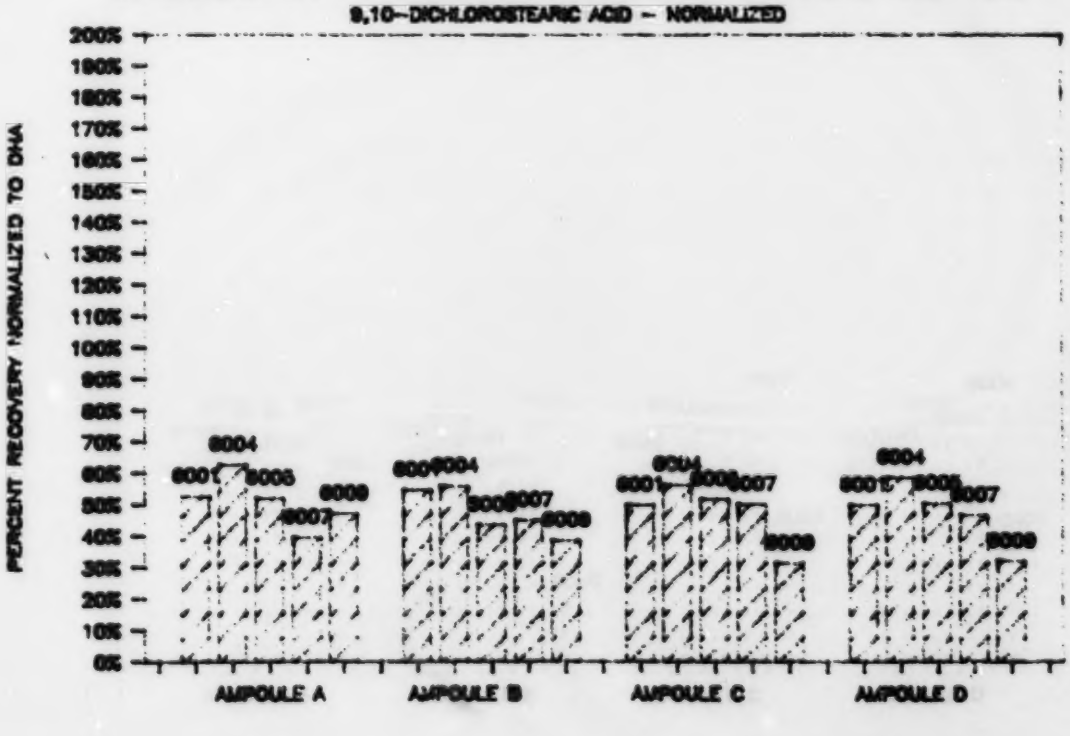


FIGURE 9: INTERLABORATORY STUDY 88–2A

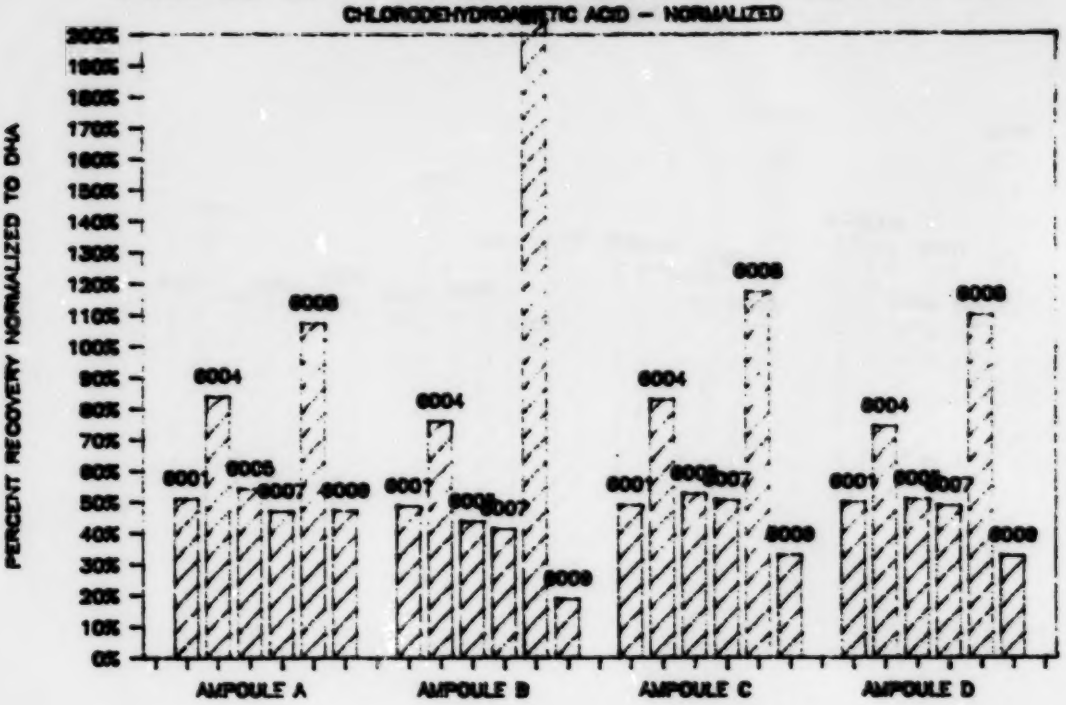


FIGURE 10: INTERLABORATORY STUDY 88–2A

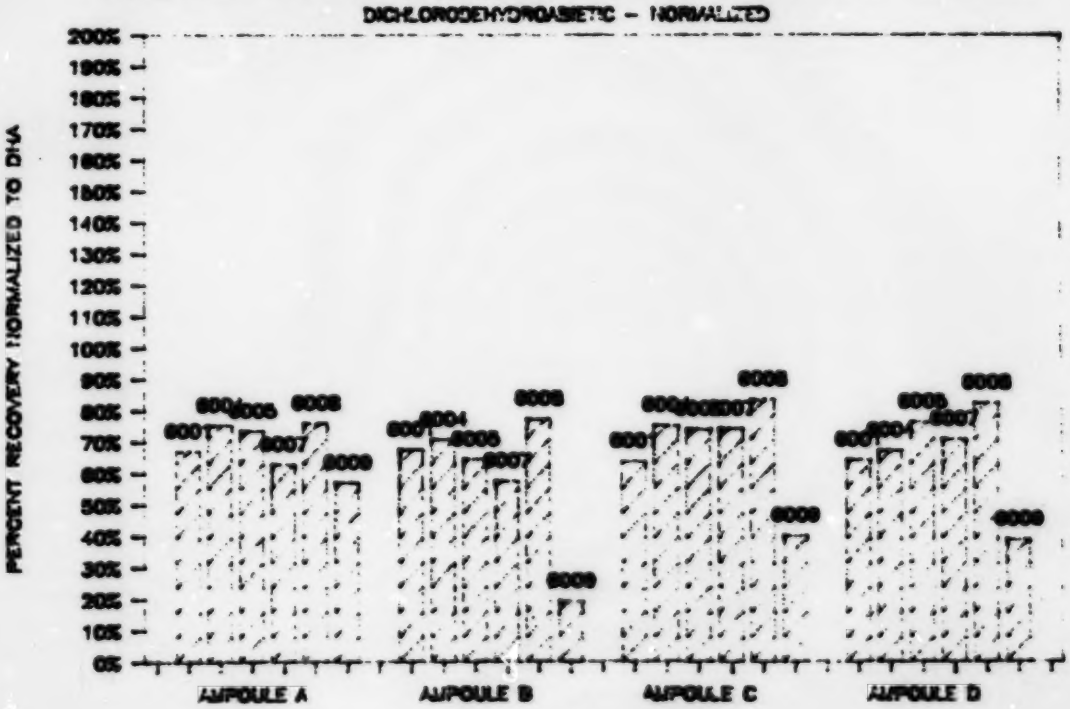
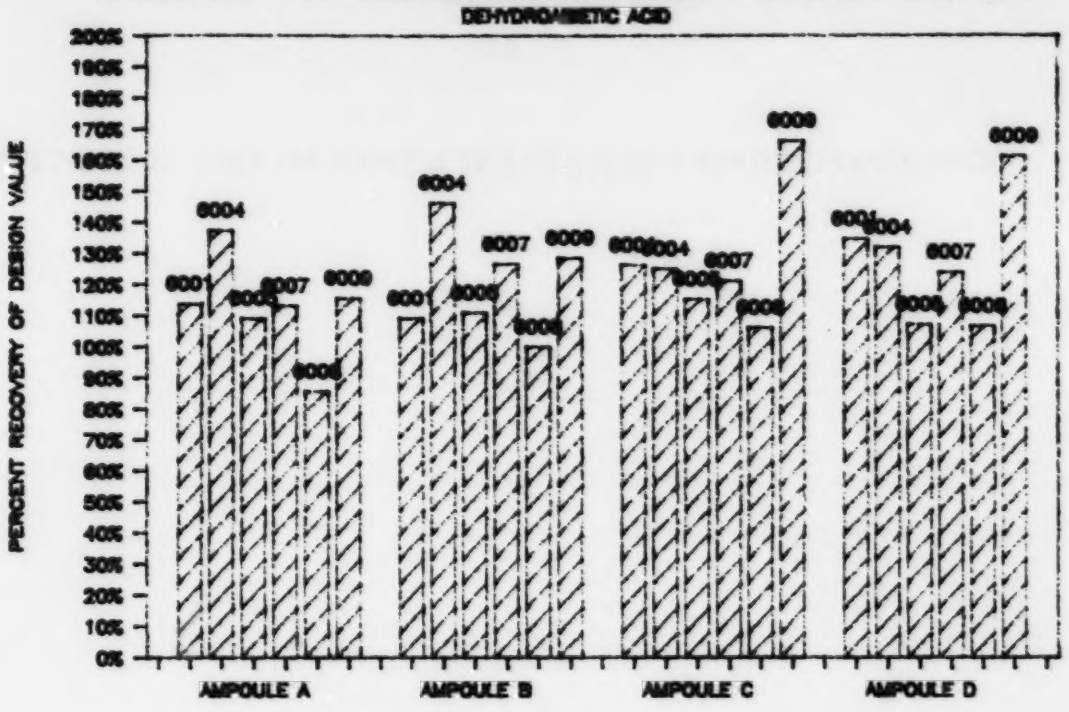


FIGURE 11: INTERLABORATORY STUDY 88-2A



8 APPENDIX 2 - LIST OF PARTICIPANTS AND CORRESPONDENCE

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Bedford Institute of Oceanography
P.O. Box 1006
Dartmouth, N.S.
B2Y 4A2
(902) 426-6191

Contact: Mr. Peter Henniger

Environmental Protection Service
Waste Water Technology Centre
867 Lakeshore Rd.
Box 5050
Burlington, Ontario
L7R 4A6
(416) 336-4633

Contact: Mr. Peter Fowlie

Ontario Ministry of the Environment
Laboratory Services Branch
Trace Organics Section
125 Resources Rd.
Rexdale, Ontario
M9W 5L1
(416) 235-5760

Contact: Mrs. Yvonne Jones

ANALYTICAL LIST FOR MISA TEST GROUPS
(Reference 2)

Test Group: 26 - Fatty and Resin Acids

Abietic Acid
Chlorodehydroabietic Acid
Dehydroabietic Acid
Isopimaric Acid
Levopimaric Acid
Neoabietic Acid
Oleic Acid
Pimaric Acid

Test Group: PP3

Dichlorodehydroabietic Acid

RESIN ACID ROUND ROBIN NOTIFICATION: May 11, 1988

INTRODUCTION

Laboratories that received notification of the Resin Acid Round Robin in December, 1987 are notified by this letter of the schedule for the inter-laboratory validation study being conducted by the Ontario Ministry of the Environment for the MISA (Municipal and Industrial Strategy for Abatement) pulp and paper Analytical Working Group. The new co-ordinator of this round robin is Sylvia Cussion and she may be contacted at (416) 235-5842.

METHODOLOGY

The previous notice (Dec. 1987) provided some background information on the MISA program and the activities of the pulp and paper Analytical Working Group. Attached to this notice is a copy of the draft method to be used for this validation study. Participating laboratories are directed to use this procedure as outlined with minimum variances. The Analytical Working Group would appreciate a report of any modifications made by the individual laboratories, as this will aid in the interpretation of the results and possibly provide improvements to the method. This report may included when reporting the analytical results of the round robin.

Prior to the commencement of the round robin, participating laboratories should follow the procedures outlined in Section 8.2 of the Draft Method to demonstrate laboratory capability. Laboratories encountering technical difficulties are urged to contact the MOE Co-ordinator for assistance.

SCHEDULE

During the week of June 6, 1988, participating laboratories will receive four (4) ampoules containing the following resin acids:

Sandaracopimaric Acid
Palustric Acid
Dehydroabietic Acid
Neoabietic Acid
Dichlorodehydroabietic Acid
Linoleic Acid
Isopimaric Acid
Levopimaric Acid
Abietic Acid
Chlorodehydroabietic Acid
Oleic Acid
9,10-Dichlorostearic Acid

The ampoules will be labelled "A", "B", "C", and "D", and will be accompanied by instructions for their use. Two (2) will be opened, methylated and injected into the gas chromatograph. Two (2) will be opened, an aliquot spiked into a specified amount of water, and processed through the entire analytical procedure. This is round one of the validation study.

Laboratories are required to perform the analysis and report the results within two (2) weeks of the reception of the ampoules. All results are to be sent to Sylvia Cussion at the following address:

Ministry of the Environment
Laboratory Services Branch
Computer Systems - QA/QC Section
125 Resources Rd.
Rexdale, Ontario, M9W 5L1

If necessary, a repeat of the above set of analyses may be requested in August or September, 1988. If the first set of results indicate successful analyses by all participating laboratories, round two of the validation study will commence in September 1988. All participating laboratories will receive a set of nine(9) spiked samples for resin acid analysis. All laboratories will receive advance notice and more details closer to the expected distribution date.

SUMMARY OF RESULTS

All participating laboratories will be assigned an identification code. All laboratories will receive a complete set of the results from round one, including a ranking for each laboratory. All laboratories will be identified only by their identification code. Conclusions drawn by the Analytical Working Group and recommendations made will also be provided to the participating laboratories.

No further notice is to be given prior to distribution of the first set of ampoules. Should a laboratory wish to withdraw from this round robin, or if there are any difficulties with the above schedule, please contact Sylvia Cussion immediately at (416) 235-5842.

Ontario Ministry of the Environment
Laboratory Services Branch
LCS-QA/QC Section
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

(416) 235-5842
FAX (416) 235-5744

June 7, 1988.

TO: PARTICIPANTS OF RFA ROUND ROBIN

Please find enclosed four (4) 5 mL amber ampoules labelled Ampoule A, Ampoule B, Ampoule C, and Ampoule D, an instruction sheet, and a results summary sheet. If you are missing any of the above items, please contact me at the above phone number immediately.

Your participation in the RFA Round Robin is greatly appreciated by the MISA Analytical Working Group. Please remember that we require each lab to adhere to the draft method as closely as possible. We ask that each lab document any variances from the method and provide copies with the results summary sheet.

As was stated in the notification distributed in May, 1988, results are expected within two weeks of reception of the ampoules. Please return the completed results summary sheet along with any notes to myself at the above address. Please contact me if there are any problems or questions re the round robin.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

ONTARIO MINISTRY OF THE ENVIRONMENT
RESIN AND FATTY ACID ROUND ROBIN
JUNE, 1988.

AMPOULE PREPARATION INSTRUCTION SHEET

Upon receipt please ensure that your laboratory received four (4) 5 mL amber ampoules labeled Ampoule A, Ampoule B, Ampoule C, and Ampoule D. Ensure that they are all intact. Store ampoules in a refrigerator at 4 degrees C until ready to process.

Do not open ampoules until ready to process.

ANALYZE ALL AMPOULES IN DUPLICATE.

Ampoule A

1. Break open ampoule carefully.

2. Add 1.0 mL of Ampoule A and 25 µL of the surrogate spiking solution (Section 6.10) to a 50 mL aliquot of reagent water in each of two separatory funnels.

3. Process the two duplicate water spikes as samples as outlined in Section 10. Do not adjust the pH of the reagent water.

4. Report the concentration of the spiked duplicates in units of µg/L (micrograms per litre).

Ampoule B

1. Break open ampoule carefully.

2. Add 1.0 mL of Ampoule B and 25 µL of the surrogate spiking solution (Section 6.10) to a 50 mL aliquot of reagent water in each of two separatory funnels.

3. Process the two duplicate water spikes as samples as outlined in Section 10. Do not adjust the pH of the reagent water.

4. Report the concentration of the spiked duplicates in units of µg/L (micrograms per litre).

Ampoule C

1. Break open ampoule carefully.

2. Add 25 µL of Ampoule C, 25 µL of the surrogate spiking solution (Section 6.10), 25 µL of the internal standard spiking solution (Section 6.7), 0.1 mL of methanol, and about 1.0 mL of diethyl ether to each of two concentration vessels.

3. Proceed with derivatization and analysis of the two duplicates as outlined in Sections 10.2 and 10.3.

4. Report the concentration of the spiking solution in Ampoule C in units of µg/mL (micrograms per millilitre).

Ampoule D

1. Break open ampoule carefully.

2. Add 25 µL of Ampoule D, 25 µL of the surrogate spiking solution (Section 6.10), 25 µL of the internal standard spiking solution (Section 6.7), 0.1 mL of methanol, and about 1.0 mL of diethyl ether to each of two concentration vessels.

3. Proceed with derivatization and analysis of the two duplicates as outlined in Sections 10.2 and 10.3.

4. Report the concentration of the spiking solution in Ampoule D in units of µg/mL (micrograms per millilitre).

ONTARIO MINISTRY OF THE ENVIRONMENT
RESIN AND FATTY ACID ROUND ROBIN
JUNE, 1988

RESULTS SUMMARY LAB #:

PARAMETER	AMPOULE A	AMPOULE B	AMPOULE C	AMPOULE D
SANDARACOPIMARIC ACID				
PALUSTRIC ACID				
DEHYDROABIETIC ACID				
NEOABIETIC ACID				
DICHLORODEHYDROABIETIC ACID				
LINOLEIC ACID				
ISOPIMARIC ACID				
LEVOPIMARIC ACID				
ABIETIC ACID				
CHLORODEHYDROABIETIC ACID				
OLEIC ACID				
9,10-DICHLOROSTEARIC ACID				

Ontario Ministry of the Environment
Laboratory Services Branch
LCS-QA/QC Section
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

(416) 235-5842
FAX (416) 235-5744

October 14, 1988.

TO: PARTICIPANTS OF RFA ROUND ROBIN 88-2A

Thank you very much for your participation in the first round of the Resin And Fatty Acid Round Robin for the MISA Analytical Working Group for the Pulp and Paper Sector. Attached is a copy of the results received from the participating laboratories, identified by lab identification code.

Ampoules A and B were prepared in methanol, and Ampoules C and D were prepared in methyl-t-butyl ether. A review of the results by the working group indicated possible differences in recovery due to the difference in solvents. As a result, member laboratories of the working group have conducted an inter-comparison to determine possible solvent effects.

Review of the solvent inter-comparison is currently underway. A decision regarding the next phase of the method development study will be made pending the results of the above inter-comparison. The Analytical Working Group hopes that all laboratories who participated in the first RFA Round Robin will be willing to participate in future round robins. All laboratories will receive notice of future round robins as they become available.

Please contact me if there are any questions.

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

FIGURE 1: INTERLABORATORY STUDY 88-2A

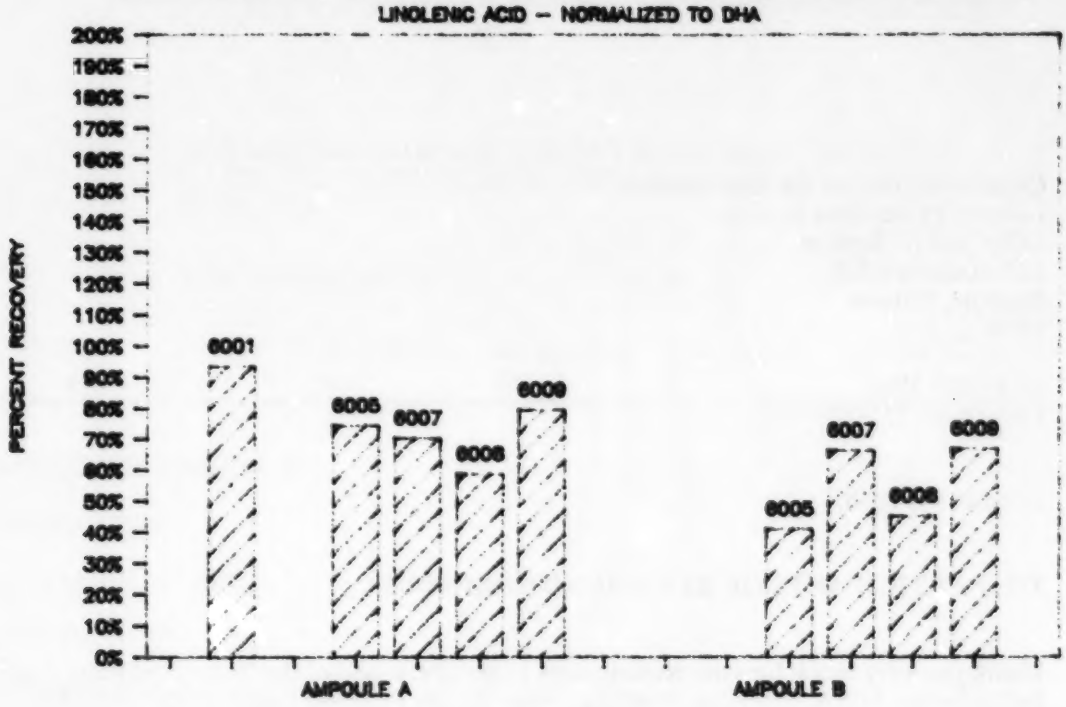

FIGURE 2: INTERLABORATORY STUDY 88-2A

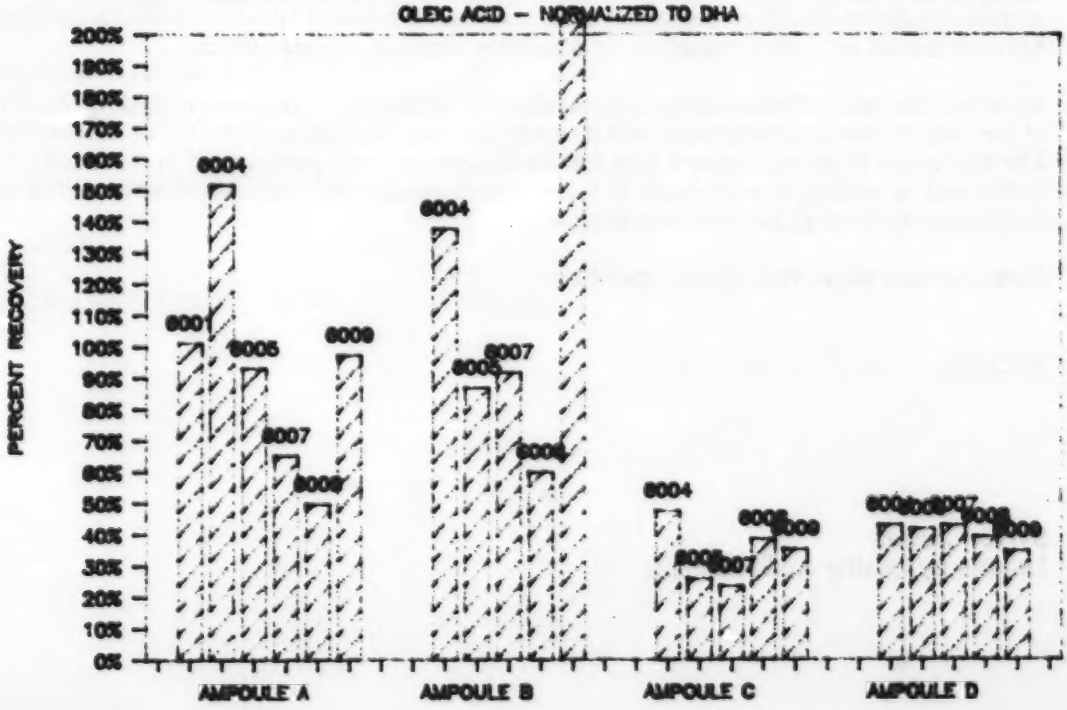

FIGURE 3: INTERLABORATORY STUDY 88–2A

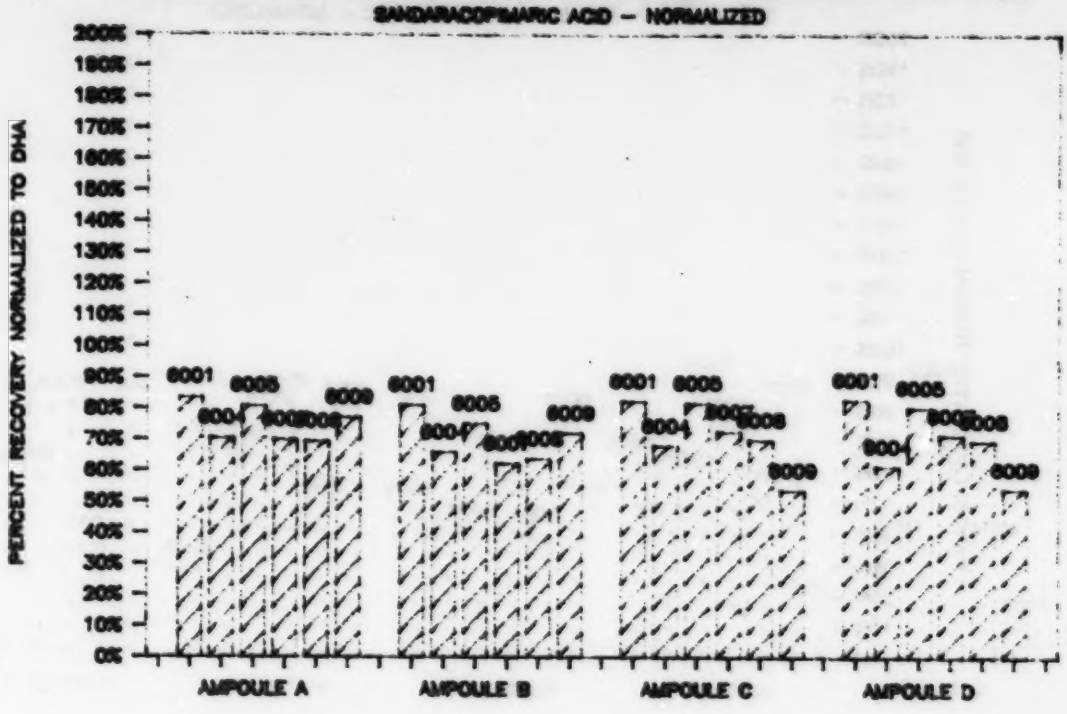

FIGURE 4: INTERLABORATORY STUDY 88–2A

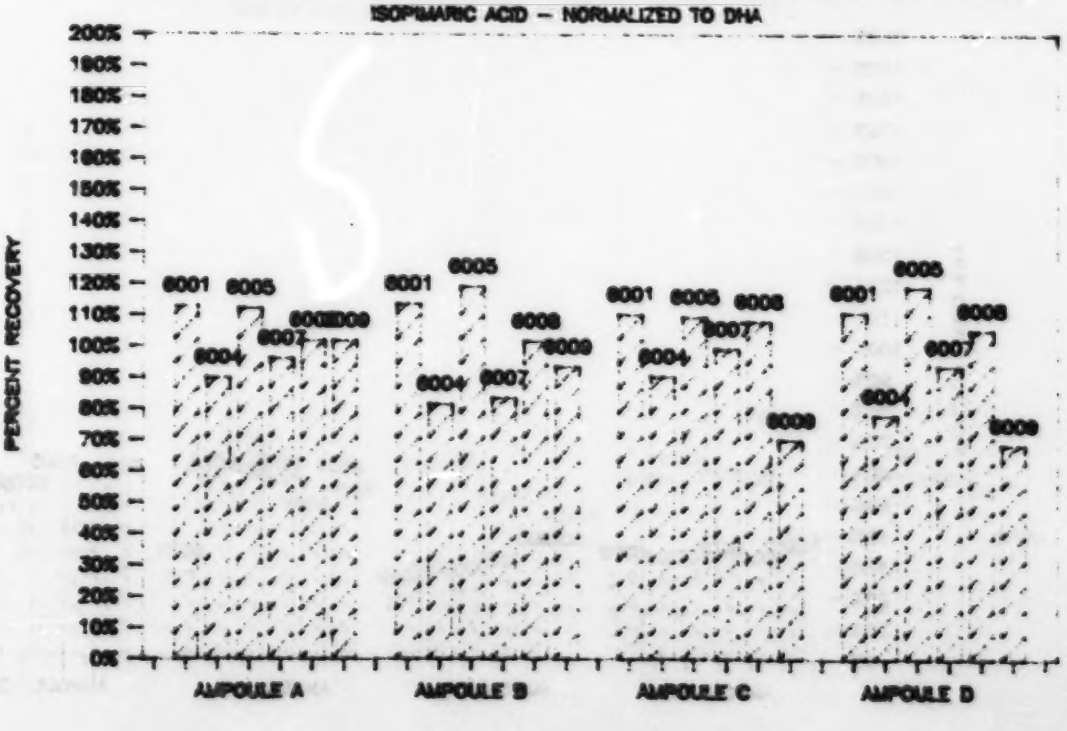

FIGURE 5: INTERLABORATORY STUDY 88–2A

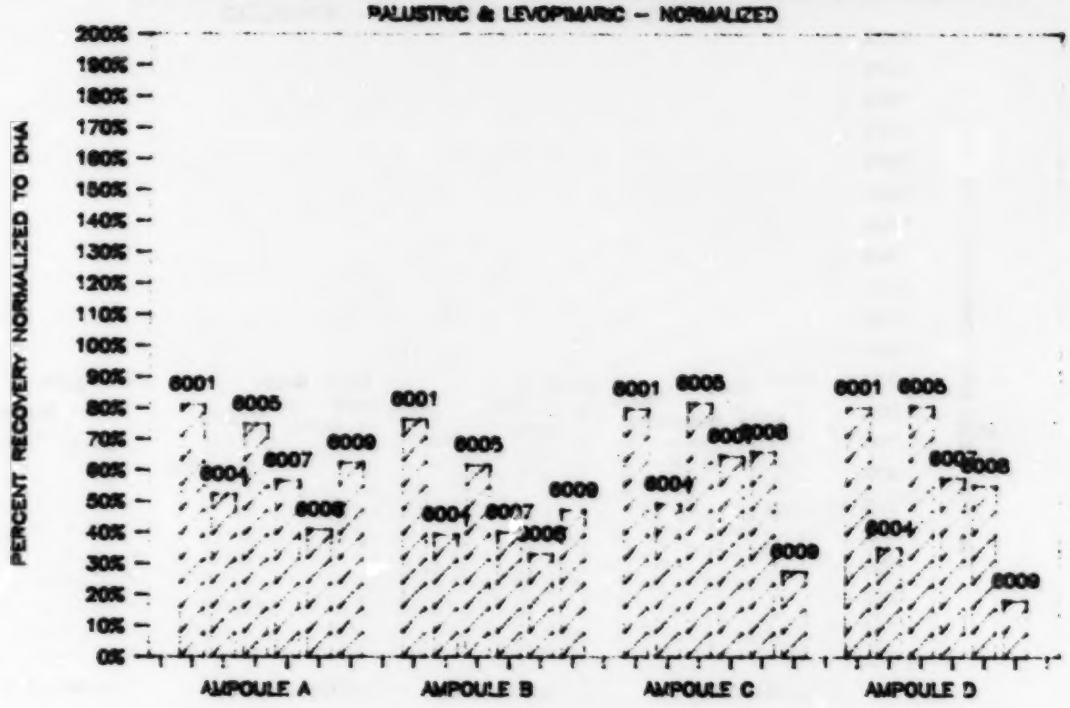

FIGURE 6: INTERLABORATORY STUDY 88–2A

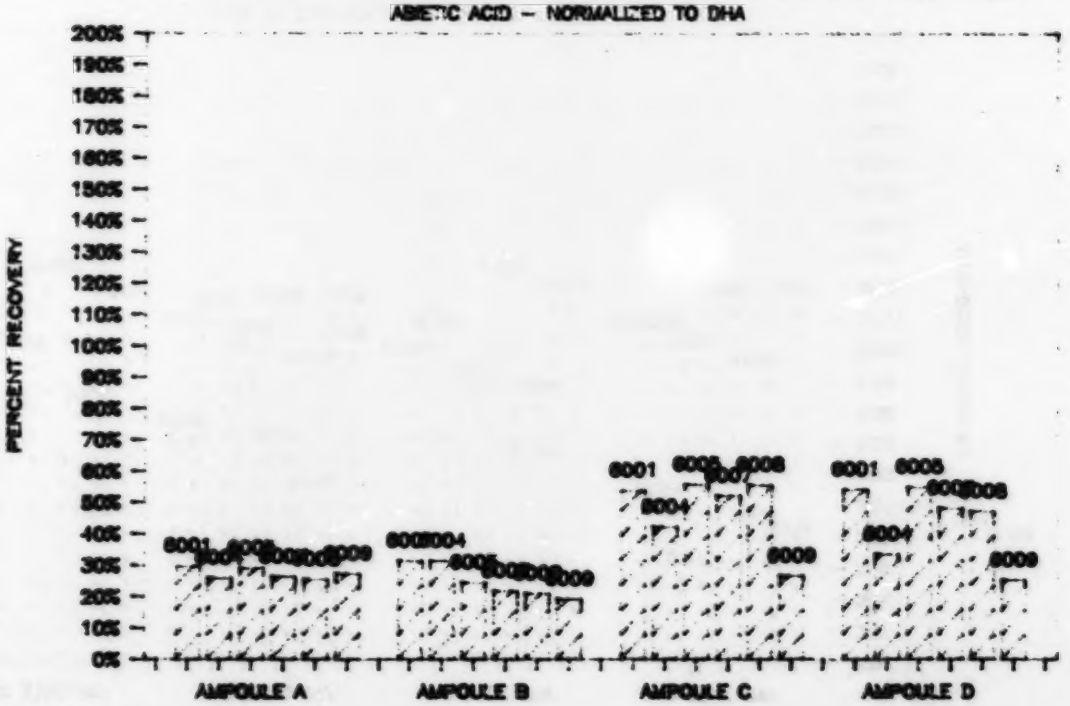

FIGURE 7: INTERLABORATORY STUDY 88–2A

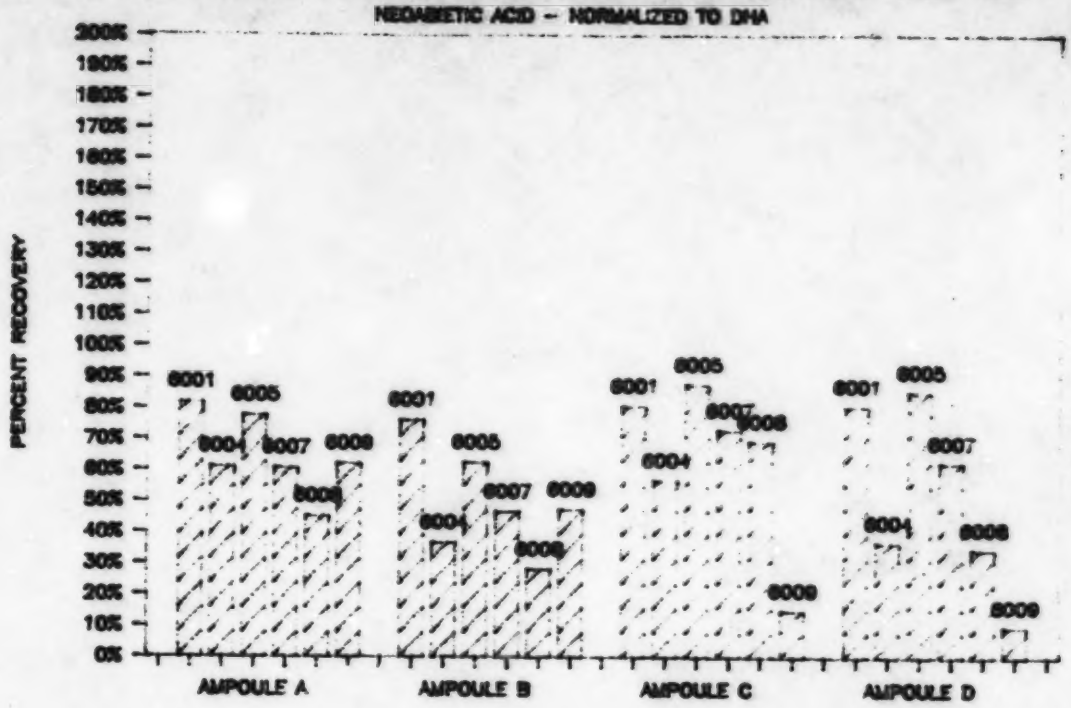

FIGURE 8: INTERLABORATORY STUDY 88–2A

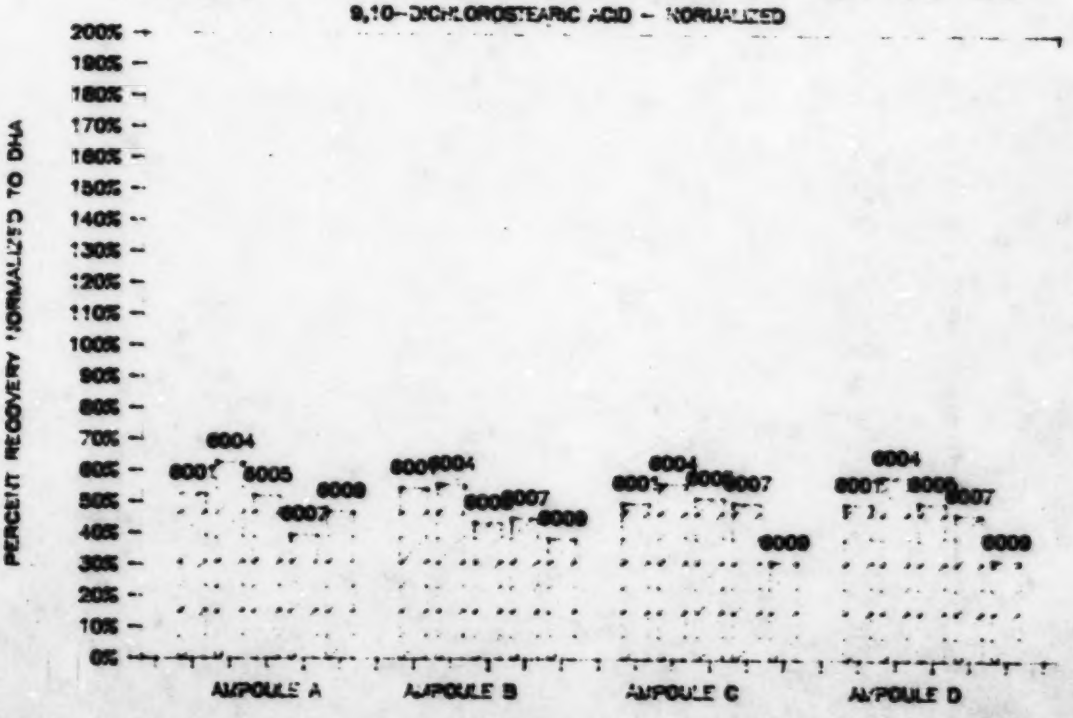

FIGURE 9: INTERLABORATORY STUDY 88--2A

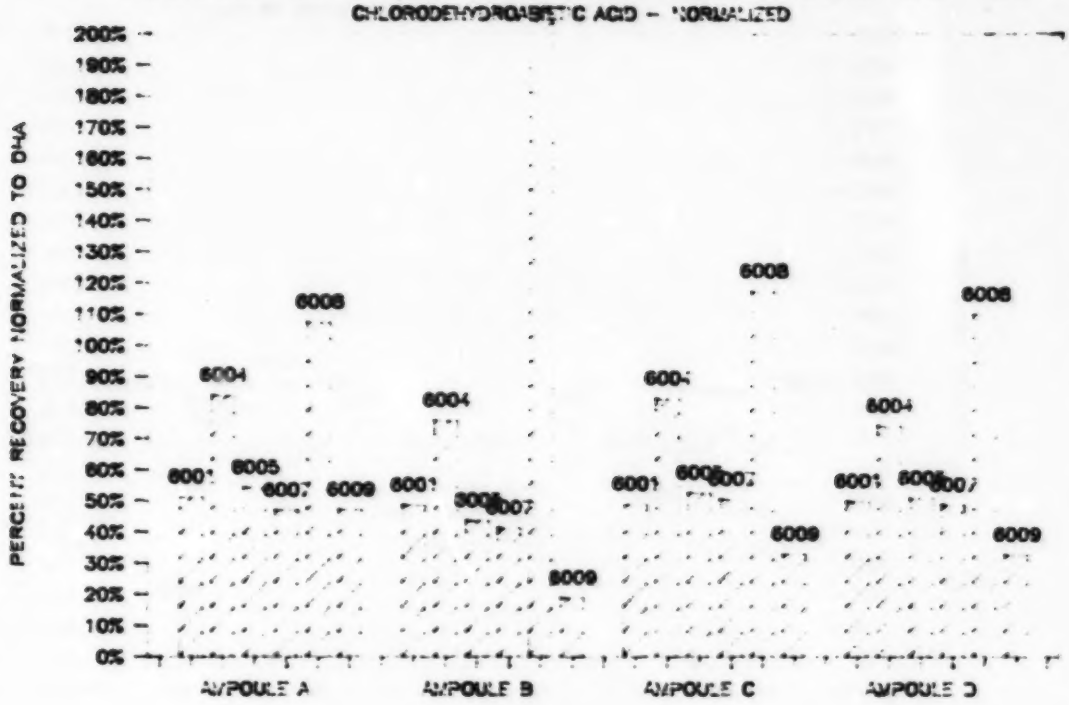

FIGURE 10: INTERLABORATORY STUDY 88--2A